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(54) Title: POLYMER VISCOSITY DEPRESSANT/SUPER COOLING THERMOPLASTIC URETHANE

(57) Abstract

The present invention is directed to multi-component compositions comprising from about 5 % to about 95 % a polyurethane formed by heating a reaction mixture comprising at least one isocyanate having a functionality less than about 2, at least one long chain polyol, at least one chain extender, and at least one plasticizer, or a thermoplastic polymer alloy comprising the reaction product of at least one polyisocyanate having a functionality of 2.2 or less, at least one substantially linear polyhydroxyl compound and/or at least one chain extender, and at least one epoxy resin, or a combination thereof, and at least another thermoplastic material selected from the group consisting of polyamide, polyurethane, ethyl vinyl acetate, polyurethane ester and polyvinyl chloride.

POLYMER VISCOSITY DEPRESSANT/SUPER COOLING THERMOPLASTIC URETHANE

Background of the invention

US patent 4,608,418 to Czerwinski *et al.* teaches hot melt urethane compositions formed from a mixture of one or more polyisocyanates, one or more hydroxyl terminated polyols, one or more chain extenders and one or more plasticizers. A hot melt composition generally is one applied in the molten state, at temperatures of about 250°-450°F (121.1°-232.2°C), and having a viscosity in that condition (Brookfield viscometer) of less than about 50,000 cps, preferably less than about 25,000 cps. When cooled to room temperature, such compositions are solids that are elastomeric in nature. These compositions are formed by heating the reactants at temperatures of at least about 330°F (165.6°C), preferably at about 350° to about 450°F (176.7°-232.2°C) for 2 or 3 hours. The compositions of this patent have been found to be excellent starting materials for use in the present invention. The disclosure of the 4,608,418 patent is hereby incorporated by reference.

US patent 4,870,142 to Czerwinski *et al.* teaches thermoplastic materials selected from the group consisting of polyamide resins made from dimer acids and diamines, ethyl vinyl acetate resins, urethane esters, urethane ethers, or polycaprolactones. The compositions of this

patent also have been found to be excellent starting materials for use in the present invention. The disclosure of the 4,870,142 patent is hereby incorporated by reference.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide compositions that have at the same time the properties of excellent adhesion, lower application temperature, lower viscositiy, and a thinner coating film. Another object is to provide methods for the preparation and application of these compositions. These and other objects of the present invention will be apparent from the following description.

SUMMARY OF THE INVENTION

The present invention is directed to multi-component compositions comprising from about 5% to about 95% of

(1a) a polyurethane according to US patent 4,608,418 formed by heating a reaction mixture comprising at least one isocyanate having a functionality less than about 2, at least one long chain polyol, at least one chain extender and at least one plasticizer, or

(1b) a thermoplastic polymer alloy according to US patent 4,870,142 comprising the reaction product of at least one polyisocyanate, at least one substantially linear polyhydroxyl compound, and/or at least one chain extender and at least one epoxy resin, or

(1c) a combination of (1a) and (1b), and

(2) from about 95% to about 5% of a thermoplastic material selected from the group consisting of polyamide resins made from a dimer acids, an ethylene vinyl acetate polymer or copolymers, a urethane ester, a urethane ether, a urethane polycaprolactone, an ethylene copolymer with acrylic acid or methacrylic acid, or a polyvinyl chloride polymer, or amorphous polypropylene.

DETAILED DESCRIPTION

As indicated previously, compositions made in accordance with the teachings of US 4,608,418 can be used as the first component (1a) of the compositions of the present invention. The first component of the urethane compositions of the present invention is, as indicated in US 4,608,418, a thermoplastic hot melt composition comprising a polyurethane having at least one plasticizer reacted therein formed by heating a reaction mixture comprising at least one isocyanate having a functionality less than about 2.2, at least one hydroxyl terminated long chain polyol, at least one chain extender and at least one plasticizer at a temperature of at least about 330°F, wherein said components are present in amounts that are within the values of the following formula:

$$\frac{A+B+C}{D} = 0.5 \text{ to about } 7.0$$

wherein A represents the equivalent weight of the long chain polyol x the moles thereof used; B represents the equivalent weight of the chain extender x the moles thereof used; C represents the equivalent weight of the isocyanate used; and D represents the grams of plasticizer.

The process for preparing the first component of the urethane compositions of the present invention generally is, as disclosed in US 4,608,418, to heat a polyurethane formed from a mixture of at least one isocyanate having a functionality less than about 2.2, at least one long chain polyol, at least one chain extender and at least one plasticizer at a temperature of at least about 330°F, wherein said components are present in an amount to meet the foregoing formula. The urethane material of the first component is based on essentially stoichiometric amounts of a diisocyanate (which insures that a thermoplastic material results) having a functionality of 2.2 or less, preferably 2.15 or less and most preferably in the range of 2.0-2.1. If the functionality is in excess of, or with certain isocyanates close to 2.2, a thermosetting material, which is excluded from the first component, results. Preferably the NCO/OH ratio in the reaction system is about 0.95 to about 1.05 as at values substantially in excess of 1.05 the reaction product tends to be non-thermoplastic.

In accordance with a preferred process of forming the first component of the compositions of the present

invention, the ingredients thereof are blended at the lowest possible temperature, the system is permitted to exotherm and, after the peak exotherm has been reached, the system is heated at about 330°F to about 450°F while agitating to complete the reaction. The reaction of the one or more plasticizers into the system is substantially completed simultaneously with attainment of the requisite temperature of at least about 330°F (165.6°C). Based on experience to date, the plasticizer cannot be extracted therefrom or is only partially extractable by common organic solvents, e.g., hexane, gasoline, motor oil, and the like, at normal end use conditions for the first component absent the second component. It is also possible, however, to simply blend all of the components, permit the blend to cure *in situ*, and then, prior to or during use, elevate the temperature to at least about 330°F. Heating time varies greatly depending upon the form of the composition. For example, assuming a substantially completely cured thin film or layer thereof (that is, one that has been permitted to cure *in situ* in place or in a container for a substantial period of time), results indicate that heating to at least about 330°F (165.6°C) for at least about two hours to form the resultant hot melt composition.

The polyisocyanate reactants useful in preparing the compositions of the present invention are aromatic, aliphatic, cycloaliphatic or aralkyl polyisocyanates

containing from about 6 to 100 carbon atoms. Although the preferred isocyanate-containing reactants contain two isocyanate groups, reactants containing more than two such groups are operative so long as the average functionality does not exceed 2.2 and the resulting urethane is thermoplastic. Blends or mixtures also are included in the foregoing definition of polyisocyanate reactants. Isocyanate terminated prepolymers which perform as diisocyanates under the processing conditions of the present invention and have an average functionality of 2.2 or less also are useful and are considered equivalent to the preferred diisocyantes. The following list is an example of polyisocyanates useful in the present invention:

4,4'-diphenylmethane diisocyanate (MDI); toluene-2,4-diisocyanate; 3-phenyl-2-ethylenediisocyanate; 1,3-naphthalene diisocyanate; 1,4-naphthalene diisocyanate; 1,5-naphthalene diisocyanate; cumene-2,4-diisocyanate; 4-methoxy-1,3-phenylene diisocyanate; 4-chloro-1,3-phenylene diisocyanate; 4-bromo-1,3-phenylene diisocyanate; 4-ethyloxy-1,3-phenylene diisocyanate; 2,4'-diisocyanato-diphenyl ether; 4,4'-diisocyanato-diphenyl ether; 2,4-dimethyl-1,3-phenylene diisocyanate; 5,6-dimethyl-1,3-phenylene diisocyanate; benzidene diisocyanate; 4,4'-diisocyanatodibenzyl; 4,6-dimethyl-1,3-phenylene diisocyanate; 1,4-anthracene diisocyanate; 9,10-anthracene diisocyanate; 3,3'-

dimethyl-4,4'-diisocyanatodiphenyl-methane; diisocyanatodiphenylmethane; 2,6-dimethyl-4,4'-diisocyanatodiphenyl; 2,4-diisocyanatostilbene; 3,3'-dimethyl-4,4'-diisocyanatodiphenyl; 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl; 2,5-fluoroene diisocyanate; 1,3-phenylene diisocyanate; methylene-bis(4-phenyl-isocyanate); 2,6-diisocyanatobenzylfuran; bis(2-isocyanato-ethyl)fumarate; bis(2-isocyanato-ethyl)carbonate; bis(2-isocyanato-ethyl)-4-cyclohexene-1,2-dicarboxylate; 1,4-tetramethylene diisocyanate; 1,6-hexamethylene diisocyanate; 1,10-decamethylene diisocyanate; 1,3-cyclo-hexylene diisocyanate; 4,4'methylene-bis(cyclohexyl diisocyanate; and tetramethylenexylene diisocyanate.

Isocyanate-terminated polyurethane prepolymers useful herein include blocked isocyanate prepolymers, such as, for example, a polyalkylene glycol or polyalkylene ether polyester, polyacetal, polyamide, polyester polyamide, or polythioether polyol, which can be reacted with an excess of a diisocyanate, such as those mentioned above, to form a suitable prepolymer with residual isocyanate groups. The prepolymers are formed in conventional manner and are generally produced by reaction materials such as mentioned above and diisocyanates at temperatures of from about 50°F to about 130°F, the reaction time being matched to the

predetermined temperature, for example two hours at about 120°F.

The substantially linear polyhydroxyl compounds with terminal hydroxyl groups include compounds of the formula HO-D-OH having a functionality of 2.2 or below wherein D is polyester, polyester amide, polyether, polyacetal, polycarbonate, or poly-N-alkylurethane. Other groups such as ester, ether, amide, urethane, or N-alkylurethane groups optionally may be present in D. The average molecular weight of the substantially linear polyhydroxyl compounds preferably from above 500 to 5000, most preferably from about 800 to about 3000. These compounds preferably have a melting point below 150°F, in particular below 110°F. It is also within the scope of the present invention to use mixtures of these compounds.

Useful compounds of formula HO-D-OH include polyesters of dibasic acids, for example adipic acid, and dialcohols, for example, ethylene glycol, propylene glycol, 1,4-butanediol; 2,5-hexanediol; 2,2-dimethyl-1,3-propanediol; 1,6-hexanediol; 2-ethyl-1,6-hexanediol; 2,2-dimethyl-1,3-hexanediol; p-bis-hydroxymethyl cyclohexane; 3-methyl-1,4-pentanediol; and 2,2-diethyl-1,3-propanediol. Mixtures of either the dibasic acid or the dialcohol, or both may be employed. It is preferred to use mixtures of diols, particularly diols containing 5 or more carbon atoms because polyesters of this kind show very high resistance to

hydrolysis. When the diols contain branched alkyl radicals, the end products also show outstanding low temperature elasticity. Polyesters obtained by polymerizing caprolactones with glycols also can be used herein.

Chain extending agents, compounds which carry at least two active hydrogen atoms per molecule and preferably have a molecular weight of from about 52 to below 500, most preferably from about 62 to about 250, are included in the reaction mixture. These compounds react with the isocyanate groups of the prepolymer to produce high molecular weight polyurethanes and polyurethane ureas by linking several isocyanate prepolymer. Examples of useful chain extending agents are the following:

> ethylene glycol; propane-1,2-diol; hexane-1,6-diol; 2-ethyl-1,6-hexanediol; dihydroxyethylurea; terephthalic acid-bis-(β-hydroxyethylamide); hydroquinone-bis-hydroxyethyl ether; naphthylene-1,5-bis-hydroxyethyl ether; 1,1-dimethyl-4-(bis-β-hydroxy yl)-semicarbazide; succinic acid; adipic acid; isophthalic acid; 1,4-cyclohexane dicarboxylic acid; ethylene diamine; hexamethylene diamine; 1,4-cyclohexane diamine; hexahydro-m-xylene diamine; m-xylylene diamine; p-xylylene diamine; bis(β-aminoethyl)-oxalamide; piperazine; 2,5-dimethyl piperazine; ethanolamine; 6-aminocaproic acid; 4,4-diaminodiphenylmethane; 4,4′-diaminodiphenyl-

dimethylmethane; 2-amino acetic acid hydrazide; 4-aminobutyric acid hydrazide; 6-aminocaproic acid hydrazide; 2-hydroxyacetic acid hydrazide; 2-aminobutyric acid hydrazide; 6-hydroxycaproic acid hydrazide; carbodihydrazide; hydracrylic acid dihydrazide; adipic acid dihydrazide; isophthalic acid dihydrazide; m-xylylene dicarboxylic acid dihydrazide; ethylene glycol-bis-carbazinic ester; butanediol-bis-semicarbazide and hexamethylene-bis-semicarbazide.

Plasticizers are also included in the reaction mixture. The plasticizer must be capable of being reacted into the polyurethane at temperatures of about 330°F (165.6°C).

Examples of such compositions include the following compositions manufactured by Advanced Resin Technology, Inc.:

Lambda™ C100-55, Lambda™ C101-35, Lambda™ C103-46, Lambda™ C200-65, Lambda™ C201-57, Lambda™ C210-50D, Lambda™ C301-75, Lambda™ L3300-80, Lambda™ L3300-85, Lambda™ L104-40 and Lambda™ L3300-90. C101-35 is a thermoplastic MDI-based, polyester urethane elastomer formed with a long chain ethylene adipate polyester diol having an average molecular weight (m.w.) of 1000 and hydroxyl number of 55. C100-55, C103-46, C200-65, C201-57, C210-50D and C301-75 are MDI-based polycaprolactone urethane elastomers, and L104-40 is an HMDI-based long chain polycaprolactone diol with an

average m.w. of 3000 and hydroxyl number of 37.4. L3300-80, L3300-85 and L3300-90 are HMDI-based polyether urethane elastomers. Of the foregoing materials, C100-55, C101-35, C103-46, C200-65, C201-57 and C301-75 are preferred.

Compositions made in accordance with the teachings of US 4,870,142 also can be used as the first component (1b) of the compositions of the present invention. Compositions according to this patent comprise the reaction product of at least one polyisocyanate, at least one hydroxyl terminated polyol and/or at least one chain extender, and at least one epoxy resin. The "urethane" materials of this patent are based on essentially stoichiometric amounts of a polyisocyanate, which insures an initially thermoplastic material, having a functionality of 2.2 or less, preferably 2.15 or less, and most preferably in the range of 2.0-2.1. While almost any polyisocyanate can be used, 4,4-diphenylmethane disiocyanate (MDI) is preferred. An example of a commercially available suitable polyisocyanate is ISONATE 143L (Dow). Isocyanate-terminated polyurethane prepolymers may be used wherein the isocyanate group is blocked with such groups as epsilon-caprolactam, methyl ethyl ketoxime, phenol, and branched alcohols such as t-butyl alcohol and isopropanol. Also, a polyalkylene glycol or polyalkylene ether polyester, polyacetal, polyamide, polyester polyamide, or polythiolether polyol may be reacted

with an excess of a polyisocyanate to form a suitable prepolymer with residual isocyanate groups. Such prepolymers are formed in conventional manner.

Examples of suitable relatively high molecular weight compounds are substantially linear polyhydroxyl compounds with terminal hydroxyl groups of the formula HO-D-OH include polyesters, polyester amides, polyethers, polyacetals, polycarbonates or poly-N-alkylurethanes, other groups such as ester, ether, amide, urethane or N-alkylurethane groups optionally being present in the foregoing compounds. The average functionality of these polyols is 2.2 or below. The molecular weight thereof preferably is from about 500 to about 5000, preferably from about 800 to about 3000 (number average). These compounds preferably have a melting point below 150°C, in particular, below 110°C. It is also possible to use mixtures of these relatively high molecular weight compounds. The substantially linear polyhydroxyl compound can be in a preformed polyisocyanate or a polyurethane prepolymer.

Specific examples of such polyhydroxyl compounds are polyesters of dibasic acids, for example, adipic acid, and diols, or mixtures of diols, for example, ethylene glycol, propylene glycol, 1,4-butanediol, 2,5-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 2-ethyl-1,6-hexanediol, 2,2-dimethyl-1,3-hexanediol, p-bis-hydroxymethylcyclohexane, 3-methyl-1,4-pentanediol, and 2,2-

diethyl-1,3-propanediol. Preferably mixtures of these diols or mixtures of diols containing 5 or more carbon atoms, because polyesters of this kind show very high resistance to hydrolysis. When the diols contain branched alkyl radicals, the polyesters also show outstanding low temperature elasticity in the end products. Polyesters obtained by polymerizing caprolactones with glycols are also suitable starting materials. Other glycols such as hydrogenated bis-phenol A, cyclohexane dimethanol, caprolactone diol (*i.e.*, the reaction product of caprolactone and ethylene glycol), hydroxyalkylated bis-phenols, polyether glycols, *e.g.*, poly(oxytetramethylene)glycol and the like also are useful. Other useful hydroxy terminated polyols include polyesters such as polyethylene glycol adipates, polyethylene butylene adipates, polyethylene glycol azelates, polyethylene butylene azelates, polycaprolactones, polycarbonates, polyethers, polybutadienes, or copolymers with acrylonitrile, styrene and the like.

The chain extending component is a compound having, per molecule, at least two active hydrogen atoms and preferably a number average molecular weight of from about 52 to about 400, most preferably from about 62 to about 250 (number average). These compounds react with the isocyanate groups of the prepolymer and build up high molecular weight polyurethane and polyurethane ureas by linking several isocyanate prepolymer molecules. Examples of useful chain

ext nding agents are, for instance, ethylene glycol, propane-1,2-diol, butane-1,4-diol, hexane-1,6-diol, 2(3)-methylhexane-1,6-diol, 3-methylhexane-1,6-diol, hydroquinone-bis-hydroxyethyl ether, and naphthylene-1,5-bis-hydroxyethyl ether.

It is preferred that the NCO/OH ratio in the reaction system be in the order of about 0.8 to about 1.1 as values substantially in excess of 1.1 tend to produce an initial reaction product that is non-thermoplastic.

The last mandatory component of the compositions of US 4,870,142 is an epoxy resin having hydroxyl function less than about 1.8, and preferably less than 1.5. The precise nature of the epoxy resin is not overly important so long as it contains sufficient hydroxyl groups to react with isocyanate groups to provide a curable, non-gelled thermoplastic polymer alloy product.

The hydroxyl functionality of the epoxy resin typically is greater than about 0.1 and must be less than about 1.8, and most preferably less than about 1.5. The equivalent weight of the epoxy resin can vary widely but most have an equivalent weight of about 100 to about 500. The molecular weight of the epoxy resin is not overly important although, assuming a direct correlation between molecular weight and the number of hydroxyl groups, if the number of hydroxyl groups is too great, cross-linking or gelation could occur and this should be avoided.

The amount of epoxy resin used according to the present invention can be defined by the range of about 0.5 to about 20, more preferably, about 0.5 to 7.0 per the following formula

$$\frac{A + B + C}{D} = \text{ca. } 0.5 \text{ to } 20$$

wherein A = equivalent weight of long chain polyol(s) x (number of equivalents thereof), and can be zero (0);

B = equivalent weight of chain extender(s), x (number of equivalents thereof), and can be zero (0);

C = equivalent weight of polyisocyanates(s) or prepolymer(s) x (number of equivalents thereof; and

D = epoxy resin(s) (number of grams thereof);

but A and B cannot both be zero.

In most instances this will mean that the epoxy resin will comprise from about 15% to about 75% of the total composition weight, more preferably, from about 20% to about 70% of the total composition weight, and most preferably from about 25% to about 65% of the total composition weight.

The compositions of component (1b) are normally formed by first blending together the long chain linear polyol, the chain extender, and the epoxy resin and, if used, any additional ingredients such as an additional thermoplastic resin, filler, etc. Blending conditions are not important and any conventional blending means can be used, though it

may be necessary to melt some materials to obtain a uniform liquid or to insure an homogeneous system. Since a solvent is not used, this is preferably accomplished at the lowest possible temperature to avoid premature reaction until the system is well mixed.

Having formed the basic ingredients, the polyisocyanate is then generally added slowly with agitation. There is no special criticality to the conditions used for polyisocyanate addition, but preferably, the lowest possible temperature to avoid premature reaction is used until the system is well mixed. Constant agitation is preferred to avoid localized pockets of materials which are not blended into an homogeneous system and, if reaction is occurring, one obviously wishes to avoid "hot spots" in the reaction system.

One of the foregoing materials (1a) or (1b), or a mixture thereof (1c), is blended with at least one other thermoplastic material as a second component of the compositions of the present invention, such as thermoplastic polyamide resins made from dimer acids, an ethyl vinyl acetate (EVA) polymer or copolymer resin, or a thermoplastic polyurethane, *e.g.* an ester or an ether, a polyester polycaprolactone, an ethylene glycol ether, an ethylene copolymer with acrylic or methacrylic acid, or a flexible or rigid polyvinyl chloride. Examples of such thermoplastic materials are the following:

a) thermoplastic polyamide resins: Versamid 930 [Henk 1] and Macromelt 6238 (Henkel),

b) EVA resins: ELVAX resins (DuPont), HL-4096-X (H.B. Fuller), 34-2771 (National Starch and Chemical Co.),

c) thermoplastic polyurethane polyesters: TEXIN (Miles) 480A, 591A, 688A, 345D, 355D, 455D, 458D and 5187,

d) polyurethane polyethers: TEXIN (Miles) 985A, 990A and 970D,

e) polyester polycaprolactones: PELLETHANE (Dow) 2102 and 2354,

f) ethylene glycol ether, polytetramethylene glycol ether, PELLETHANE (Dow) 2103 and 2363,

g) ethylene copolymers with acrylic or methylacrylic acids, several of which are commerically available,

h) polyvinyl chlorides, several of which are commercially available both in flexible and original forms.

Component (2) of the compositions of the present invention is at least one other thermoplastic material selected from the group consisting of polyamide resins made from a dimer acids, ethyl vinyl acetate resins, polyurethane esters, polyurethane ethers, a polyurethane polycaprolactones, and a flexible or rigid polyvinyl chlorides.

At least one material from each of the foregoing component groups in percentages of from about 5% to about

95% of the first (1a, 1b or 1c) to from about 95% to about 5% of the second (2), preferably from about 15% to about 85% of the first to from about 85% to about 15% of the second, and most preferably from about 30% to about 70% of the first to from about 70% to about 30% of the second, are used according to the present invention, depending upon the materials and the desired final viscosity. The materials are mixed and the resulting blend or dry blend is processed in an appropriate mixing equipment such as, for example, an extruder, a sigma mixer, a planetary mixer, and the like, under a process that controls heat, pressure and shear energy in the equipment to insure proper mixing without overheating the mixture. Those skilled in the art will understand that the processing temperatures will vary with the materials in the blend and their percentages. In general, any combination of shear and temperature to melt the materials is satisfactory and will usually be a temperature of about 250-400°F (121.1-204.4°C), usually not over 425°F (218.4°C), with minimal shear conditions.

The product from the mixer can be underwater pelletized, strand pelletized, crushed, granulated or otherwise particle reduced. It is then ready to be further processed in adhesive dispensing equipment, film extruder, hot melt dispenser closed pail unloader, or similar equipment for handling heated plastic materials.

Once the first component (1a, 1b or a mixture of both,

1c) in the blend is melted, a liquid melt system occurs. Upon heating with temperature and shear, the mixture develops into a low viscosity multi-component system that readily flows under pressure as a hot liquid. Even under cooling conditions, the flow of material generates heat from movement and this helps keep the (A) component from freezing. When the thermoplastic material (B), under cooling, starts to solidify, it is, nevertheless, kept moving in the flow of the first (A) component. This feature is seen as a depression of the freezing point, and explains the ability of the compositions of the present invention to coat heat sensitive materials at temperatures below the starting process temperatures. The thinness of the films involved, as thin as 1 mil or less, and the heat sink effect of using the container as the mandrel in applying the label enhances the performance of the system in enabling the material to cool thereby improving adhesive properties. As any significant increase in mass of materials will slow this process down, for high speed label applications, the thinner the mass, and the greater the heat sink, the better the composition will perform, up to the limits of mechanical properties of the composition.

The compositions of the present invention have many advantageous properties among which can be mentioned:

a) depressed viscosity thereby enabling the composition to be applied without using solvents at lower viscosity with

asier processing conditions with the introduction of heat and shear,

b) due to the lowering of viscosity with introduction of heat and shear, the composition can be cooled below the original melting temperatures but still be of sufficiently low viscosity to be applied as a coatable film,

c) the ability to be cooled sufficiently to enable application to heat sensitive/heat shrink materials, either single films or laminates, tubing, polypropylene heat shrink labels and films, films of polystyrene or foam polystyrene, polyvinyl chloride and blends, polyethylene, and various other blends of olefinic polymers without distorting the film,

d) sufficient temperature resistance to withstand the rigors of commercial pasteurization processes as normally found in the beer and beverage industries,

e) sufficient thermal resistance to withstand for short periods of time higher process temperatures normally encountered in the beverage/food industries in hot filling containers, *i.e.*, as high as 200-210°F (93.3-98.9°C) for 10-15 minutes, without permitting separation of the materials bonded together such as a label on an aluminum can, glass bottle, polyethylene terephthalate bottle or other containers used in this industry,

f) lowered freeze point of thermoplastic materials and mixtures thus permitting lower processing temperatures and

the ability to apply materials at coating weights without the use of solvents,

g) superior "green strength", that is to say, the strength of an adhesive while hot, under which condition many adhesives have poor adhesion and only develop acceptable adhesive strength when cooled.

The following examples illustrate the present invention without, however, limiting the same thereto.

EXAMPLE 1

Thirty grams of an MDI-based polycaprolactone urethane elastomer, Lambda™ C103-46 (Advanced Resin Technology), and 100 g of polytetramethylene glycol ether (PTMEG), PELLATHANE 2103-70A (Dow), are dry blended in a dessicant drier following the recommendations of the manufacturer of the PTMGE. After the materials are well and evenly dispersed, and protected from moisture during blending, they are extruded in a 0.75 inch (1.90 cm) Killion extruder using the following extruder heat profile starting at the feed zone, feed hopper water cooled throat, zone 1 - 385°F (196.1°C), zone 2 - 380°F (193.3°C), zone 3 - 370°F (187.8°C), die 350°F (176.7°C). During the blending the viscosity of the PTMEG Decreases. Under continuous running conditions, the melt temperature is similarly reduced compared to the original melt temperature of the PTMEG. If the extruded product is re-extruded, its melt temperature will be

similarly lowered, depending, of course, upon similar percentages and shear involved.

EXAMPLE 2

The procedure of Example 1 is repeated using a mixture consisting of 25 g of Lambda™ C200-65 and 75 g of a polyester-based polyurethane, ESTANE 58144. A similar reduction in viscosity and melt temperature of the extrudate is obtained.

EXAMPLE 3

The procedure of Example 1 is repeated using a mixture consisting of 75 g of Lambda™ C301-35 and 25 g of a polyamide resin (Versamid 930, Henkel). A similar reduction in viscosity and melt temperature of the extrudate is obtained.

EXAMPLE 4

An adhesive composition for use in hot melt adhesive applications is prepared from equal parts by weight of C301-75 and an ethylene vinyl acetate resin, 34-2771 (National Starch and Chemical Company). The composition is melted in standard hot melt equipment at a temperature of 250°F to 300°F (121.1°C to 148.9°C). Once the material has become molten, it has a sufficiently low viscosity to be pumpable through heat hoses and the like to the coating/application

heads. During this movement the material is cooled to a lower temperature of approximately 200°F (93.3°C) but still maintains a viscosity sufficiently low to permit delivery to the coating/application heads. At the point of application, the material can still be applied as a thin continuous film and during application to the heat shrink polypropylene film/heat sensitive film, the film does not change or distort as the adhesive composition is being applied.

Once applied to the label and/or container, the adhesive composition develops enough "green strength" to hold the label securely during the heat shrinking operations. That is, the adhesive is strong enough and heat resistant enough to go through the heat shrinking station in which a stream of high heat forced air is directed at the top and bottom of the container for a short period of time to shrink the label without degrading the film itself.

After a period of time of from a few hours to about 12 hours, and in some cases up to as much as 48 hours, the container is filled via the commercial pasteurization process. The adhesive maintained its integrity and prevented the label from moving during the commercial pasteurization process, and meets the performance requirements of commercial pasteurization as found in the beer/beverage industry. In addition, once cooled, the adhesive performs well as a standard label adhesive.

What is claimed is:

1. A composition for use as a hot melt adhesive comprising (1a) a polyurethane having at least one plasticizer reacted therein formed by heating a reaction mixture comprising at least one isocyanate having a functionality less than about 2.2, at least one long chain polyol, at least one chain extender and at least one plasticizer at a temperature of at least about 330°F (165.6°C), wherein said components are present in amounts sufficient to meet the following formula:

$$\frac{A + B + C}{D} = 0.5 \text{ to about } 7.0 \text{ wherein}$$

wherein A represents the equivalent weight of the long chain polyol x the moles thereof used;

B represents the equivalent weight of the chain extender x the moles thereof used;

C represents the equivalent weight of the isocyanate x the moles thereof used; and

D represents the grams of plasticizer, or

(1b) a thermoplastic polymer alloy comprising the reaction product of at least one polyisocyanate having a functionality of 2.2 or less, at least one substantially linear polyhydroxyl compound and/or at least one chain extender, and at least one epoxy resin, or

(1c) a combination of (1a) and (1b), and

(2) at least one other thermoplastic material selected from the group consisting of a polyamide resin made from a dimer acid, an ethyl vinyl acetate resin, a polyurethane ester, a polyurethane ether, a polyurethane polycaprolactone, and a flexible or rigid polyvinyl chloride.

2. The composition according to claim 1 wherein the isocyanate in a) and the polyisocyanate in b) each has a functionality of 2.15 or less.

3. The composition according to claim 1 wherein the isocyanate in a) has a functionality of from about 2.0 to about 2.1.

4. The composition according to claim 1 wherein the isocyanate in a) is a diisocyanate.

5. The composition according to claim 1 wherein the isocyanate in a) contains from 6 to about 100 carbon atoms.

6. The composition according to claim 1 wherein the long chain polyol in a) and the substantially linear polyhydroxyl compound in b) each has an average molecular weight of from above 500 to about 5000.

7. The composition according to claim 1 wherein the chain extender in a) and in b) has an average molecular weight of from about 52 to about 400.

8. The composition according to claim 1 wherein the NCO/OH ratio is about 0.95 to about 1.05.

9. The composition according to claim 1 wherein the

plasticizer in a) comprises from about 20% to about 70% of the total composition weight.

10. The composition according to claim 1 wherein the long chain polyol in a) and the substantially linear polyhydroxyl compound in b) each has an average functionality of 2.2 or below.

11. The composition according to claim 1 wherein the epoxy resin in b) has an hydroxyl functionality of less than about 1.8.

12. The composition according to claim 1 wherein the epoxy resin in b) has an hydroxyl functionality of less than about 1.5.

13. The composition according to claim 1 wherein the epoxy resin in b) is selected from the group consisting of bis-phenol epoxy resins, aliphatic epoxy resins, novolac epoxy resins, brominated epoxy resins and isocyanurate epoxy resins.

14. The composition according to claim 1 wherein the amount of the epoxy resin in b) is defined by the range of from about 0.5 to 7.0 per the following formula:

$$\frac{A + B + C}{D} = \text{about } 0.5 \text{ to } 7.0$$

wherein A = equivalent weight of long chain polyol(s) x (number of equivalents thereof), and can be zero (0);

B = equivalent weight of chain extender(s), x (number of equivalents thereof), and can be zero (0);

C = equivalent weight of polyisocyanates(s) or prepolymer(s) x (number of equivalents thereof; and

D = epoxy resin(s) (number of grams thereof);

but A and B cannot both be zero.

15. The composition of claim 1 wherein the substantially linear polyhydroxyl compound has a functionality of equal to or less than 2.2 and the chain extender has a molecular weight of about 52 to less than 500.

16. A method of preparing the composition of claim 1 comprising dry blending a polyurethane of composition (a) and/or a thermoplastic polymer alloy of composition b) with at least one other thermoplastic material selected from the group consisting of a polyamide resin made from a dimer acid, an ethyl vinyl acetate resin, a polyurethane ester, a polyurethane ether, a polyurethane polycaprolactone, and a flexible or rigid polyvinyl chloride, and subjecting the blended material to a combination of heat and shear sufficient to melt the blend.

17. A method according to claim 16 wherein the heat is from about 250°F to about 400°F (121.1 to about 204.4°C).

18. A method of applying a coating comprising melting the composition of claim 1 by subjecting it to a combination of heat and shear sufficient to melt the blend, passing the melted blend to the coating/application heads, and applying the melted blend as a thin continuous film to a heat shrink

film.

19. A method according to claim 18 wherein the heat shrink film is polypropylene, polystyrene or foamed polystyrene.

20. A method of applying a coating comprising melting the composition of claim 1 by subjecting it to a combination of heat and shear sufficient to melt the blend, passing the melted blend to the coating/application heads, and applying the melted blend as a thin continuous film to a heat sensitive film.

21. A method according to claim 20 wherein the heat shrink film is a polypropylene, polystyrene or foamed polystyrene.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07228

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08F 8/30
US CL :525/127, 129, 457, 458
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/127, 129, 457, 458

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,248,731 (TEUMAC ET AL) 28 September 1993, see Abstract.	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"E" earlier document published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search 07 SEPTEMBER 1994	Date of mailing of the international search report 14 NOV 1994
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